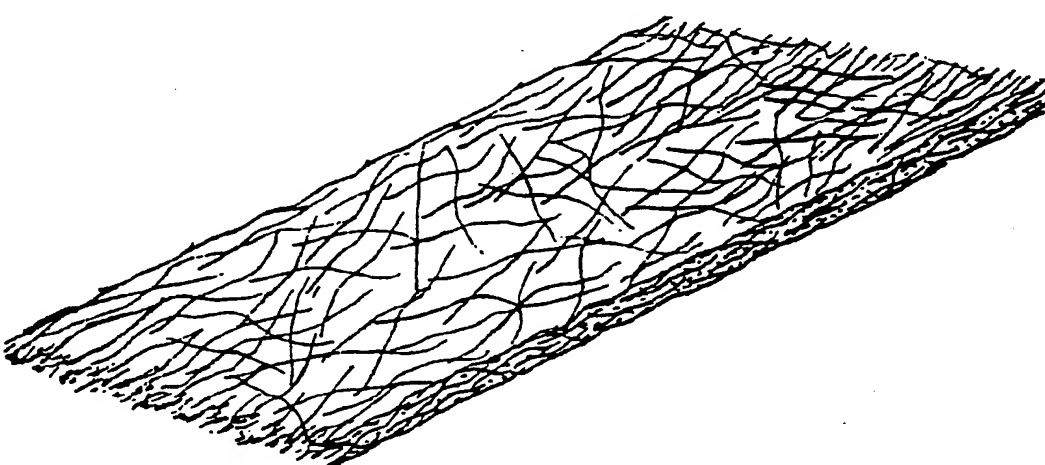




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US87/00095 (22) International Filing Date: 15 January 1987 (15.01.87) (31) Priority Application Number: 820,485 (32) Priority Date: 17 January 1986 (17.01.86) (33) Priority Country: US (71) Applicant: BATTELLE MEMORIAL INSTITUTE [US/US]; 505 King Avenue, Columbus, OH 43201-2693 (US). (72) Inventor: HISCOCK, Donald, F. ; 4214 East Lea, Co- lumbus, OH 43214 (US). (74) Agents: WIESMANN, Klaus, H. et al.; Battelle Memo- rial Institute, 505 King Avenue, Columbus, OH 43201-2693 (US).		(81) Designated States: AT (European patent), BE (Euro- pean patent), CH (European patent), DE (European patent), FI, FR (European patent), GB (European pa- tent), IT (European patent), JP, LU (European pa- tent), NL (European patent), NO, SE (European pa- tent). Published <i>With international search report.</i>
(54) Title: WET-LAID, NON-WOVEN, FIBER-REINFORCED COMPOSITES CONTAINING STABILIZING PULP  (57) Abstract Process for forming a fiber-reinforced, heat-fusible polymeric composite wherein a dilute aqueous slurry of reinfor- cing fibers and solid heat-fusible polymeric particles are deposited on a foraminous support, and the resulting mat de-wa- tered and heat-fused. The improvement in forming an unfused mat of improved integrity and for improving the processa- bility of the dilute aqueous slurry comprises incorporating into the aqueous slurry a stabilizing amount of pulp fibers characterized as being less than about 10 mm in length, being flexible, and having broomed ends (e.g. micro-fibrillar).		

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Wet-laid, non-woven, fibre-reinforced composites containing stabilizing pulp.

Background of the Invention

The present invention relates to fiber-reinforced polymeric composites prepared by an aqueous slurry process and more particularly to improved composites and an improved process for making such composites.

5 Composite materials represent a fast growing segment of the plastics industry because of their capability of providing the high strength and stiffness exhibited by metals, but at a greatly reduced part weight. Composite materials additionally can display resistance to chemicals and provide a cost savings in many applications. Parts fashioned from fiber-reinforced polymeric sheet composites can exhibit high mechanical
10 properties due to the fiber reinforcement with the polymer matrix providing the appropriate shape, resistance to chemicals, and like properties. Most currently-available composites are formed from thermosetting polymers including polyesters, epoxies, vinyl esters, polyimides, and the like. Thermosetting polymers, while providing adequate performance in many
15 applications, do suffer from a number of disadvantages. Accordingly, recent development in this field has included techniques for permitting thermoplastic sheet composites to be manufactured and especially to be stamped to make ultimate parts of desired shape, strength, and like properties.

20 Heretofore, polymeric sheet composites have been made by a variety of processes including injection molding, dry-laid mat formation, extrusion, and a variety of additional techniques well known to those skilled in this art field. One process for composite sheet formation which has received little attention is the wet forming or wet-laid process wherein composites are
25 made in a process very similar to a conventional Fourdrinier paper making process. An example of such wet forming process is set forth in U.S. Pat. No. 4,426,470 wherein a dilute aqueous slurry of solid heat fusible organic polymers, reinforcing fibers, and latex binder are flocculated with a polymeric flocculant, collected in the form of a mat, dewatered, and dried.
30 Thereafter, the dried mats can be heat-consolidated. The use of a specific polymeric flocculant apparently is aimed at overcoming the flocculation

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problems encountered in dispersing solid polymeric particles and reinforcing fibers in water. Despite these attempts at overcoming the problems inherently associated with forming fiber-reinforced polymeric composites by a wet-forming process, need in the art for a simplified process yet exists.

5

Broad Statement of the Invention

The present invention provides a simple, yet effective means for greatly improving the making of fiber-reinforced polymeric composites by a wet-forming process and provides a superior unfused composite mat. The process of the present invention is an improvement in process for forming a fiber-reinforced, heat-fusible polymeric composite wherein a dilute aqueous slurry of reinforcing fiber and heat-fusible polymeric particles are deposited on a foraminous support, the resulting mat dewatered, and heat-fused. The improvement for forming an unfused mat of improved integrity and in improving the processing of the dilute aqueous slurry comprises incorporating into said aqueous slurry a stabilizing amount of pulp fibers. The pulp fibers are micro-fibrillar so that their length generally will be less than about 10 mm and more often will range from between about 1 and 6 mm. The pulp fibers additionally are flexible and have broomed ends. The resulting mat is characterized by a uniform and homogeneous content of solid polymeric particles dispersed throughout the reinforcing fibers. Such mat possesses improved unfused sheet strength and improved integrity.

Advantages of the present invention include a dilute aqueous slurry which is non-clumping (i.e. in which the reinforcing fibers are more resistant to entanglement), is homogeneous, and in which the solids are readily dispersed. Another advantage is that the formation of the unfused sheet or mat proceeds readily due to the homogeneity of the dilute aqueous slurry from which the solids are being deposited. A further advantage is that the resulting unfused mat possesses improved sheet strength and is superior in integrity to a mat formed from the same ingredients sans stabilizing pulp. These and other advantages will be readily apparent to those skilled in the art based upon the disclosure contained herein.

Brief Description of the Drawings

Fig. 1 is a representation of an unfused mat in which the dilute aqueous slurry did contain a stabilizing amount of pulp fibers.

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Fig. 2 is a representation of a wet-laid mat wherein the dilute aqueous slurry did not contain any pulp fibers.

The drawings will be described in greater detail in connection with the remaining description of the invention.

5

Detailed Description of the Invention

The wet-forming or wet-laid process of the present invention is similar to a paper making process in a variety of respects. Initially, the inventive process operates by formation of a dilute aqueous slurry which includes reinforcing fiber, solid polymeric particles, and stabilizing pulp, although a variety of conventional additives may additionally be included in the slurry. Broadly, the dilute aqueous slurry contains from between about 0.01 to about 5% non-volatile solids by weight, though generally the slurry is restricted to about 1% non-volatile solids by weight or less. Advantageously, the slurry should contain from between about 0.01 and about 1% non-volatile solids by weight. It will be appreciated that the solids content of the slurry, as well as a variety of additional factors in the process, will vary depending upon whether a batch (hand sheet) or continuous process is utilized in forming the unfused sheet or mat of the present invention. In order for processability of the dilute aqueous slurry, it is important that the reinforcing fibers do not clump (become entangled) and that the slurry is homogeneous in content. At a solids content of about 0.2 wt-% or greater, the reinforcing fibers become entangled. Quite unexpectedly, the addition of pulp fibers to the slurry resulted in non-clumping of the fibers as well as improved homogeneity of the slurry. Additionally, the slurry was easy to work with and maintained a smooth, uniform texture. Presently, no precise explanation for the effect displayed by the stabilizing pulp fibers has been satisfactorily set forth.

As to the mat or sheet which is formed from the dilute aqueous slurry, the inventive mat possesses integrity and sheet strength far beyond that realized by a conventional counterpart sheet, i.e. a sheet identical in composition but for the inclusion of the stabilizing pulp. The sheet also is characterized by a uniform texture and even dispersion of density. In this regard, reference is made to the drawings. The unconsolidated or unfused sheet represented in Fig. 2 resulted from the wet-forming of glass fiber (about 1/2 inch in length and 13.5 microns in diameter) and polybutylene terephthalate resin (50% by weight of each). The unfused mat is very loose in

texture and is reminiscent of "angel hair". As such, it possesses little integrity and much of the solid polymeric particles are lost from the bulk of the mat. Such mat should be contrasted with that represented at Fig. 1 which was formed from glass fiber (1/2 inch in length and 9 microns in diameter), PBT resin, and aramid(Keylar)pulp (54.5 wt-% glass fiber, 40 wt-% resin, and 5.5 wt-% pulp). The inventive mat is characterized by a uniform texture, is substantially thinner in thickness, and is more reminiscent of "felt". Additionally, little loss of solid polymeric particles results from handling of this inventive mat. Truly, a unique achievement has resulted by the addition of a small, yet effective proportion of stabilizing pulp solids to the dilute aqueous slurry.

As to the materials which comprise the aqueous slurry from which the inventive mat is wet-formed, utilization of a furnish (as used in the paper making genre) with the consistency of pulp is utilized. The pulp solids or pulp fibers are composed of organic materials and are characterized as being micro-fibrillar, flexible, and possessing broomed ends. That is, the pulp is not rod-like as is the characteristic of conventional reinforcing fibers. Even more remarkable is that but a minor proportion of the pulp need be added to the dilute aqueous slurry in order to achieve the unique benefits exhibited by the present invention. That is, in making static hand sheets of the composite, generally only between about 0.5-1% by weight of the stabilizing or dispersing pulp is required, though higher proportions (e.g. up to 5-10 wt-%) certainly do not adversely effect the processing of the slurry nor the ultimate properties of the mat. Even though continuous processing on a Fourdrinier or the like machine has yet to be undertaken, it is believed that conventional furnish proportions as low as about 0.1-0.2% by weight of the pulp should function. In terms of volume percent of stabilizing pulp, between about 3 and 7 volume percent of pulp has been tested and found to be satisfactory. Mats containing up to 60 wt-% pulp have been made where the pulp was used as a matrix material, though only small quantities of pulp are required as a processing aid. It will be appreciated that the proportion of stabilizing pulp necessarily must be adjusted to take into account the type of reinforcing fiber, the size and aspect ratio of the reinforcing fiber, the kind of pulp utilized, and additional factors which should be apparent to those skilled in this field of art. The stabilizing pulp solids should possess a size coextensive with the size of cellulosic pulp which is used in making paper. Thus, the stabilizing pulp can

range on up to about 10 mm in length, though generally the pulp will range from between about 1 and 6 mm in length.

The composition of the pulp is not a limitation on the present invention as a wide variety of organic pulps have been successfully utilized in accordance with the precepts of the present invention. The pulp material may be heat-fusible and of the same or different composition from the solid polymeric particles. Pulps successfully evaluated include, for example, polyolefins, (e.g. polyethylene and polypropylene), cellulose, and aramid fibers. So long as the pulp solids possess the characteristics of being microfibrillar, flexible, and broom ended, the pulp material should function effectively and efficiently in the process of the present invention.

The reinforcing fibers generally will range from about 1/4 inch to about 1 inch in length. That such longer fibers can be handled by the present invention and not clump is a unique achievement. The composition of the fibrous reinforcement is not a limitation in that conventional glass, carbon (graphite), various polymers (e.g. polyesters), metal fibers, and the like find utility in the present invention. Such fibers must be non-woven for use in the process of the present invention for forming a wet-laid, non-woven mat composite. Of necessity is that the reinforcing fibers be compatible or dispersible in water. Those fibers which do not readily disperse in water may be surface treated with various wetting agents or surfactants for improving their dispersibility in water. The proportion of reinforcing fiber in the dilute aqueous slurry generally will range from between about 10 and 60% by volume.

The heat-fusible, solid polymeric particles also must be water dispersible for forming a homogeneous dilute aqueous slurry. Thus, the polymeric particles optionally may be treated for improving their water dispersibility (e.g. pre-disposing polyether ether ketone particles in isopropanol). Another important consideration in choice of polymer involves the density of the solid polymeric particles. The density of the polymeric particles must be such that the particles will not float nor sink at too great a rate in order for a homogeneous slurry to be formed. Thus, size attrition of oversized particles for improving the buoyancy of "heavy" particles may be utilized on occasion. Additionally, specially-formed particles may be required in order for adjusting the density of the solid polymeric particles (e.g. the formation of neutral density talc-filled polypropylene particles). A final restriction on the solid polymeric particles involves their size. That is,

the size of the solid polymeric particles must not be so small that they are not retained on the foraminous layer or screen on which the solids from the slurry are deposited. Thus, some minimum size must be adhered to, though this size necessarily will depend upon the particular screen utilized. A
5 practical maximum particle size of about 1 mm was encountered since larger sized particles were recalcitrant to flow under consolidation conditions; though no theoretical maximum particle size as a processing aid should obtain for the polymeric particles, provided that the polymeric particles can be stably dispersed in the dilute aqueous slurry.

10 The kind or type of fusible polymeric particles also is not a restriction, viz, it is only important that the particles be fusible into a continuous film by the action of heat. Thus, the solid polymeric particles may be thermosetting or may be thermoplastic depending upon the intended use of the composite or other factors. For thermoplastic materials, a variety of
15 homopolymers and copolymers may be used including for example, vinyl resins, olefins, phenoxy resins, polyimides, polyethers, polyether imides, aromatic polyesters, polyamides, polysulfones, polycarbonates, polyacetals, polyethylene oxide resins, polystyrenes, acrylics, neoprenes, polyphenylene oxide resins, cellulose esters, and the like. For thermosetting polymers,
20 include, for example, polyesters, epoxies, vinyl esters, polyimides, polyurethanes, acrylics, and the like. Virtually any kind of thermoplastic or thermosetting solid polymeric particles as has been used in forming reinforced composites heretofore may be utilized to advantage in the present invention. The proportion of powdered resin content generally will
25 range from about 10 to about 90 volume percent.

The composites of the invention also may optionally contain a variety of other ingredients. Minor amounts, for example, of fillers such as silicon dioxide, calcium carbonate, magnesium oxide, wollastonite, mica, or the like may be incorporated into the composition of the present invention, provided
30 that the water dispersibility and density of such filler ingredients are properly adjusted and maintained. Additionally, various pigments or dyes may be added to impart opacity and/or color. Additional optional ingredients include anti-oxidants, UV stabilizers, bacteriacides, and the like.

As noted above, while the continuous processing on a Fourdrinier
35 machine has not yet been utilized, it is believed that such process can be readily adapted to the present invention, as those skilled in the art will appreciate. With respect to the batch or hand sheet wet-forming process as

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has been practiced, the following procedure has been determined to be preferred, though certainly can be modified as is necessary, desirable, or convenient in conventional fashion. Preferably, the pulp is dispersed in water followed by the addition of reinforcing fibers thereto. Finally, an aqueous slurry of the solid polymer particles are incorporated and the slurry diluted to the desired concentration, e.g. less than 1% solids by weight typically.

Next, the slurry is mixed thoroughly with a low shear stirrer or the like and the slurry dumped into the sheet forming unit. The water then is evacuated through the foraminous layer or screen in conventional paper-making fashion. The mat formed on the screen possesses improved integrity and unfused sheet strength, so that its handling is made much easier. Next, the mat is removed from the unit and excess water squeezed therefrom, e.g. by passing the mat against an absorbent felt between press rolls. Finally, the remainder of the water is removed by drying, e.g. in an oven, heated air, or like conventional manner. Finally, the composite is consolidated by heat and pressure. With respect to the consolidation step, it was determined that improved performance could be realized by first applying heat to the composite prior to applying pressure. Such procedure is believed to have application to wet-laid composites as well as dry-laid composites. Consolidation temperatures and pressures are conventional depending upon the materials utilized as is well known to those skilled in the art.

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CLAIMS

1. In a process for forming a fiber-reinforced, heat-fusible polymeric composite wherein a dilute aqueous slurry of reinforcing fibers and solid heat-fusible polymeric particles are deposited on a foraminous support, the resulting mat dewatered, and heat-fused, the improvement in forming an unfused mat of improved integrity, which comprises:
5 incorporating into said aqueous slurry a stabilizing amount of pulp fibers characterized as being less than about 10 mm in length, being flexible, and having broomed ends.
10
2. The process of claim 1 wherein said pulp fibers are characterized as being from between about 1 and 6 mm in length.
- 15 3. The process of claim 1 wherein said pulp is heat-fusible.
4. The process of claim 1 wherein said pulp is selected from a polyolefin, a cellulose, and an aramid.
20
5. The process of claim 1 wherein said stabilizing amount of said pulp fibers ranges from between about 3% and 7% by volume of the solids in said slurry.
- 25 6. The process of claim 1 wherein said polymeric particles are thermosetting or thermoplastic.
7. The process of claim 1 wherein said polymeric particles are selected from the group consisting of vinyls, olefins, phenoxys, polyimides, polyethers, polyether imides, aromatic polyesters, polyamides, polysulfones, polycarbonates, polyacetals, polyethylene oxides, polystyrenes, acrylics, neoprenes, polyphenylene oxides, cellulose esters, epoxies, polyurethanes, and mixtures thereof.
30
8. The process of claim 1 wherein the proportion of said polymeric particles ranges from between about 10% and 90% by volume of the solids in said slurry.
35

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9. The process of claim 1 wherein said reinforcing fiber is composed of glass, carbon, or a polymer.

10. The process of claim 1 wherein said reinforcing fibers range in
5 length from about 1/4 inch to about 1 inch.

11. The process of claim 1 wherein the proportion of said reinforcing
fibers ranges from between about 10% and 60% by volume of the solids
content of said slurry.

12. The process of claim 1 wherein the solids content of said slurry
ranges from between about 0.01% and 5% solids by weight.

13. The process of claim 12 wherein said slurry concentration ranges
15 from between about 0.01% and 1% solids by weight.

14. An unfused, fiber-reinforced, heat-fusible polymeric composite
which comprises:

(a) between about 3 and 50 volume percent of pulp fibers
20 characterized as being less than about 10 mm in length, being flexible, and
having broomed ends;

(b) between about 10 and 60 volume percent reinforcing fibers
ranging in length from between about 1/4 and 1 inch; and

(c) between about 10 and 90 volume percent of solid, heat-
25 fusible polymeric particles.

15. The unfused mat of claim 14 wherein said fiber is composed of
glass, carbon, or a polymer.

16. The unfused mat of claim 14 wherein said polymeric particles
30 are thermosetting or thermoplastic.

17. The unfused mat of claim 14 wherein said polymeric particles
are selected from the group consisting of vinyls, olefins, phenoxys,
35 polyimides, polyethers, polyether imides, aromatic polyesters, polyamides,
polysulfones, polycarbonates, polyacetals, polyethylene oxides, polystyrenes,
acrylics, neoprenes, polyphenylene oxides, cellulose esters, epoxies,
polyurethanes, and mixtures thereof.

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18. The unfused mat of claim 14 wherein said fiber is composed of a polyolefin, a cellulose, or an aramid.

5 19. The unfused mat of claim 14 which has been subjected to heat consolidation.

20. The unfused mat of claim 14 wherein said pulp fibers range from between about 3 and 7 volume percent.

1/1

FIG. 1

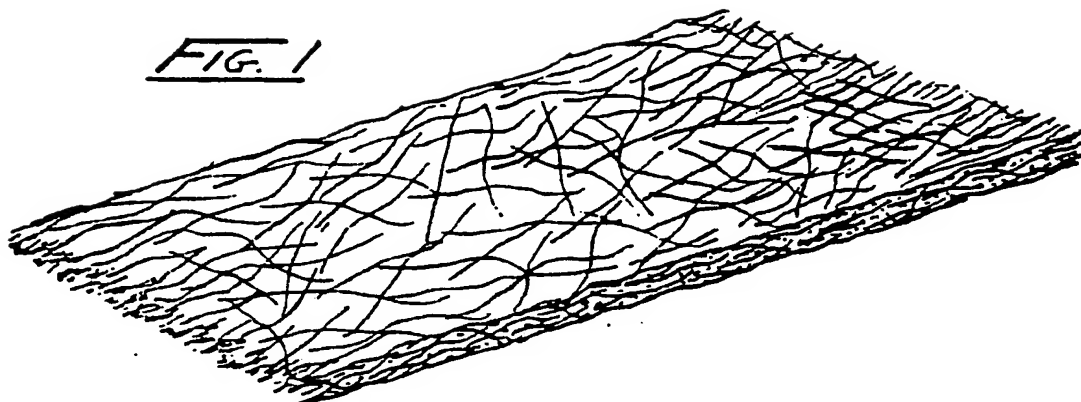
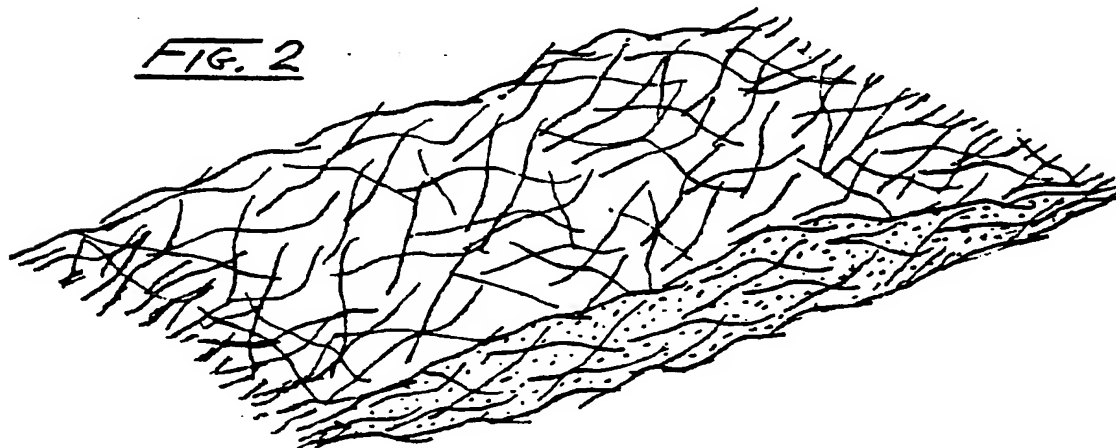


FIG. 2



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 87/00095

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁴ : D 21 H 5/00																							
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 30%; border-bottom: 1px solid black; padding: 5px;">Classification System</td> <td style="border-bottom: 1px solid black; padding: 5px;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">IPC⁴</td> <td style="padding: 5px;">D 21 H</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	IPC ⁴	D 21 H																	
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black; padding: 5px;">Category ⁹</th> <th style="width: 70%; border-bottom: 1px solid black; padding: 5px;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%; border-bottom: 1px solid black; padding: 5px;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">EP, A, 0039292 (ARJOMARI-PRIOUX) 4 November 1981, see pages 1-11 --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-20</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">FR, A, 2507123 (ARJOMARI-PRIOUX) 10 December 1982, see claims 1-6, 10, 11; page 1, line 27 - page 4, line 35; example 7 --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1, 2, 4, 6-19</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">US, A, 4279696 (J.L. PIERSON) 21 July 1981 see the whole document --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1, 2, 4-8, 14, 16, 17, 19</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">GB, A, 1597369 (K. HOLBEK) 9 September 1981 see claims 1-3, 5, 15, 17-20, 39, 45, 46; pages 16-26, 28, 29 --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1, 2, 4, 6-12, 14-19</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">US, A, 2962414 (H.F. ARLEDTER) 29 November 1960, see examples 1, 3 --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1, 2, 4, 6-12, 14-19</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">US, A, 2962415 (H.F. ARLEDTER) 29 November 1960, see example 2 --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1, 2, 4, 6-12, 14-19</td> </tr> </table> <div style="margin-top: 10px;"> <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div> </div>			Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	EP, A, 0039292 (ARJOMARI-PRIOUX) 4 November 1981, see pages 1-11 --	1-20	X	FR, A, 2507123 (ARJOMARI-PRIOUX) 10 December 1982, see claims 1-6, 10, 11; page 1, line 27 - page 4, line 35; example 7 --	1, 2, 4, 6-19	X	US, A, 4279696 (J.L. PIERSON) 21 July 1981 see the whole document --	1, 2, 4-8, 14, 16, 17, 19	X	GB, A, 1597369 (K. HOLBEK) 9 September 1981 see claims 1-3, 5, 15, 17-20, 39, 45, 46; pages 16-26, 28, 29 --	1, 2, 4, 6-12, 14-19	X	US, A, 2962414 (H.F. ARLEDTER) 29 November 1960, see examples 1, 3 --	1, 2, 4, 6-12, 14-19	X	US, A, 2962415 (H.F. ARLEDTER) 29 November 1960, see example 2 --	1, 2, 4, 6-12, 14-19
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IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="padding: 5px;">3rd April 1987</td> <td style="padding: 5px;">12 MAY 1987</td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;">International Searching Authority</td> <td style="border-bottom: 1px solid black; padding: 5px;">Signature of Authorized Officer</td> </tr> <tr> <td style="padding: 5px;">EUROPEAN PATENT OFFICE</td> <td style="padding: 5px;"> L. ROSSI </td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	3rd April 1987	12 MAY 1987	International Searching Authority	Signature of Authorized Officer	EUROPEAN PATENT OFFICE	L. ROSSI													
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
X	Abstract Bulletin of the Institute of Paper Chemistry, volume 55, no. 4, October 1984, (Appleton, Wisconsin, US), see page 512, no. 4868, & JP, A, 156100/83 (NITTO SPINNING CO.) 16 September 1983	1,2,4,6- 8,10-12, 14,16,18, 19
X	Chemical Abstracts, volume 99, no. 20, 14 November 1983, (Columbus, Ohio, US), see page 92, abstract 160238f, & RO, A, 74878 (C.I. SIMIONESCU et al.) 30 September 1980	1,2,4,6- 9,11,14- 18

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 87/00095 (SA 15901)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 14/04/87

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0039292	04/11/81	FR-A- 2481707 JP-A- 57028135 AT-B- E8676 CA-A- 1174015 US-A- 4645565	06/11/81 15/02/82 15/08/84 11/09/84 24/02/87
FR-A- 2507123	10/12/82	None	
US-A- 4279696	21/07/81	None	
GB-A- 1597369	09/09/81	NL-A- 7713424 DE-A- 2753651 FR-A- 2377883 BE-A- 861518 JP-A- 53094605 CA-A- 1113661 SE-A- 7713454	06/06/78 08/06/78 18/08/78 05/06/78 18/08/78 08/12/81 04/06/78
US-A- 2962414		None	
US-A- 2962415		None	

For more details about this annex :
see Official Journal of the European Patent Office, No. 12/82